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(54) **Membrane/hydrocracking process for improved feedstock utilization in the production of reduced emissions gasoline**

(57) A method for maximizing the utilization of hydrocarbon feedstock in the production of reduced emissions gasoline comprises fractionating 2 cat cracker effluent 1 into a reduced emissions gasoline blending stream 3, a heavy cat naphtha stream 5 and a light cat cycle oil stream 7, feeding the heavy cat naphtha, optionally with some light cat cycle oil, to a selective membrane extraction unit 6 wherein a saturates-rich retentate 9 and an aromatics; polar- and heteroatom-rich permeate 12 are produced, optional hydrotreating 10 the retentate to produce high quality jet fuel or distillate and hydrocracking 8 the aromatics rich permeate with the light cat cycle oil stream 7 to produce hydrocrackate 13 and gas 14.
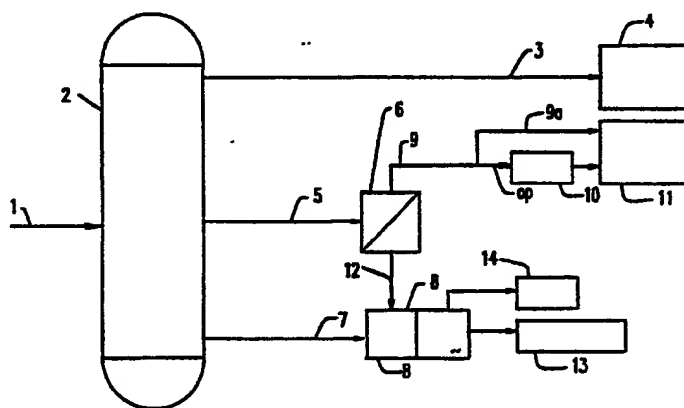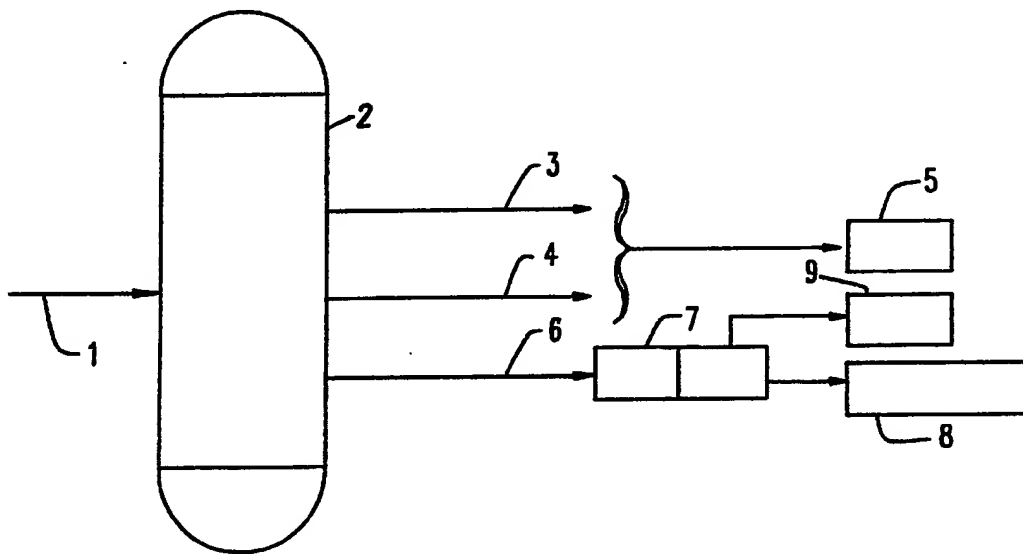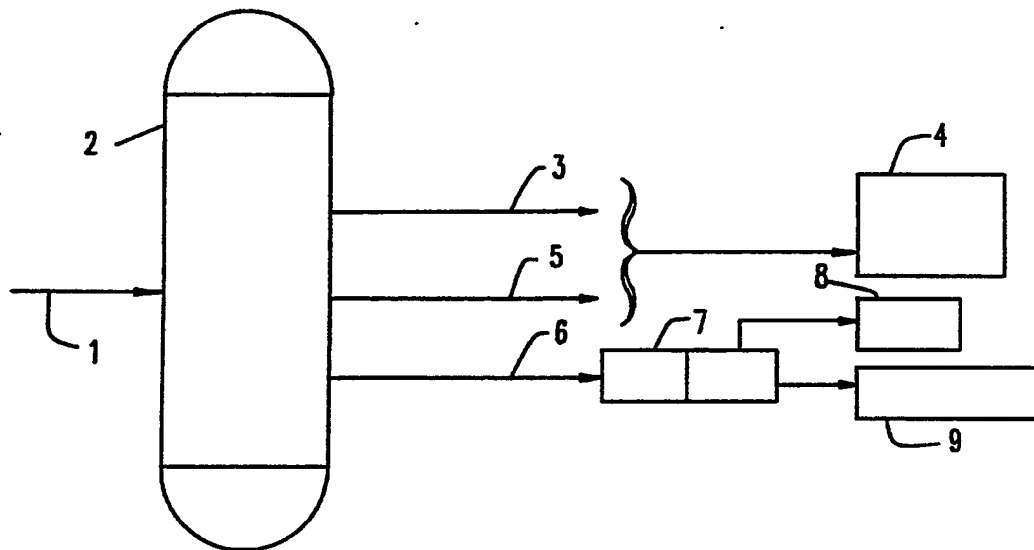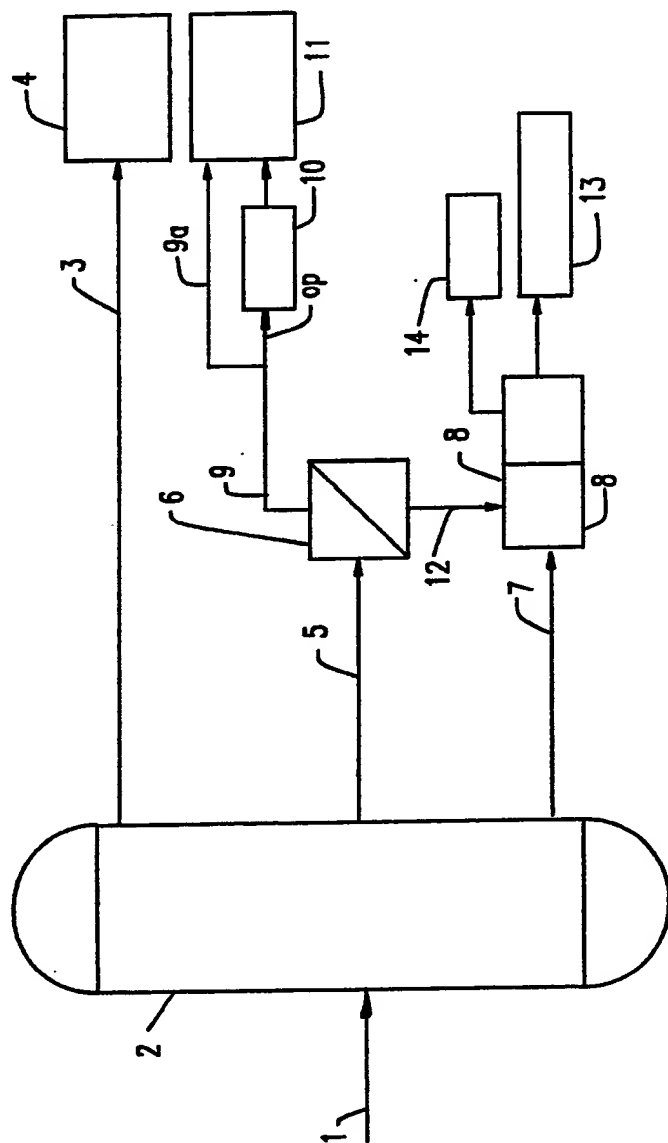
FIG. 3

GB 2 268 186 A

FIG. 1

FIG. 2

FIG. 3

Background of the Invention

Field of the Invention

The present invention is a process for the improved utilization of hydrocarbon feed stock in the production of low emission gasoline from cat cracker effluent. The process comprises (1) fractionating cat cracker effluent into a reduced emissions gasoline blending stream, a heavy cat naphtha stream and a light cat cycle oil, (2) passing the heavy cat naphtha stream and optionally a part of the light cat cycle oil to a selective membrane separation unit, (3) recovering from the membrane separation unit an aromatics, sulfur and other heteroatom rich permeate and a saturate rich retentate, (4) passing the saturates rich retentate to the jet or distillate pool, optionally following treatment in a hydrotreater and (5) passing the aromatics/sulfur/heteroatom rich permeate to a hydrocracker for conversion into hydrocrackate and gas.

Because of the restrictions which will be placed on reduced emissions gasoline regarding aromatics, polars and heteroatom content, heavy cat naphtha, which has traditionally been blended into the mogas pool, will no longer be allowed to be so used. Valuable molecules would be lost or converted into lower value product if the HCN was sent to the hydrocracker and converted into hydrocrackate and gas. The present process permits the maximum recovery of valuable molecules from the HCN by use of membrane separation wherein a retentate suitable as jet or distillate after optional hydrotreating is recovered and the objectionable aromatics, sulfur, and other heteroatom molecules are recovered as a permeate which is suitable as hydrocracker feed for conversion into hydrocrackate and gas.

Description of the Figures

Figure 1 is the current typical gasoline production scheme.

Figure 2 presents a method for producing reduced emissions gasoline by excluding heavy cat naphtha from the mogas pool.

Figure 3 presents the present invention wherein reduced emissions gasoline - produced by the valuable molecules in the HCN are recovered as high value jet and distillate via membrane separation and hydrotreating.

The Present Invention

Production of reduced emissions gasoline is the current goal of environmentalists and governments in pursuit of improved air quality.

The production of reduced emissions gasoline will require that certain components currently present in gasoline such as aromatics sulfur and other heteroatom molecules be limited in the gasoline pool.

Current gasoline production typically involves the use of certain fractions of cat cracker effluent as gasoline feed stock.

The cat cracker effluent fractions are used because straight run gasoline secured by the distillation of crude cannot meet demand. Cat cracker effluent contains significant quantities of hydrocarbons boiling in the gasoline range. Cat cracker effluent is fractionated to recover the fraction boiling in that range. The cat cracker effluent is fractionated into fractions boiling in the naphtha range (about 450°F-) and distillate boiling range (about 450°F+) also called light cat cycle oil. As currently practiced the fractionation of cat cracker effluent produces a gasoline blending component containing aromatic hydrocarbons. These components are primarily the light and intermediate cat naphtha fractions which are blended directly into the mogas pool and heavy cat naphtha and light cat cycle oil. A portion of the heavy cat naphtha fraction has been blended into the mogas pool because of its high aromatics content which contributes significantly to the octane level of the pool. The presence of aromatics, however are objectionable in reduced emissions gasoline.

In future blending schemes this heavy cat naphtha, because of its aromatic, sulfur and other heteroatom molecule content, will be excluded from the mogas pool.

Consequently the HCN along with the LCCO would typically be treated in a hydrocracker in the presence of hydrogen to produce hydrocrackate and gas. The hydrocrackate can be blended to the reduced emissions mogas pool with or without intermediate processing, such as catalytic reforming.

This, however is not an economically attractive alternative because some of the more valuable hydrocarbon molecules present in the HCN are lost in the hydrocracking process and converted to lower value hydrocrackate or lost as low value gas. In addition, present hydrocracker capacity may not be sufficient to accommodate the additional volumes of HCN which will become available for processing once the use of HCN as a mogas blending component is prohibited. This would necessitate expensive grass roots hydrocracker construction or, equally expensive hydrocracker expansion which would also entail the additional expense of securing the required quantities of hydrogen demanded by such expansions.

The present invention maximizes hydrocarbon feed utilization in reduced emissions gasoline production by recovering the high value hydrocarbon components present in the HCN and LCCO prior to hydrocracking.

In the present invention the cat cracker effluent is still fractionated into light and intermediate cat naphtha which is suitable for blending directly into the reduced emissions gasoline mogas pool and HCN.

The HCN, boiling in the 300°F+ range (300-450°F) which cannot be directly blended into mogas along with a portion of the light cat cycle oil is sent to a selective membrane separation unit. This is accomplished not by physically blending a portion of LCCO into the HCN but by broadening the HCN cut point thus, to include a portion

of the LCCO in the HCN, the fractionator cut point is set higher so that the lower boiling portion of which is now classified as LCCO passes into the HCN, that is, the naphtha fraction would boil in the, e.g., 550°F range with the HCN being a broader cut fraction boiling in the 300°F to 550°F range rather than the 300° - 450°F range. The membrane unit separates the HCN/LCCO stream into an aromatics/-sulfurs/heteroatom rich permeate and a saturates rich retentate.

The saturates rich retentate may optionally be hydrotreated at 150°C to 400°C, preferably 250°C to 350°C, 50 to 2500 psig, preferably 100-500 psig, 0.1 to 10 LHSV, preferably 1 to 5 LHSV, 50 to 1500 scf H_2/bbl, preferably 100-500 scf H_2/bbl over a catalyst active for hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation and/or aromatics and/or olefin hydrogenation, said catalysts which might contain Ni/Mo, Co/Mo, Ni/Co/Mo, Co/W or Ni/W or other transition metals on alumina, silica or zeolite supports. Pure or plant hydrogen may be used.

This saturates rich retentate (optionally hydrotreated) is useful as high value jet blending stock or as distillate.

The permeate is sent to hydrocracking performed at 200 to 500°C, preferably 300 to 400°C, 100 to 2500 psig, preferably 500 to 1500 psig, 0.1 to 10 LHSV, preferably 1 to 5 LHSV and 500 to 10,000 SCF H_2/bbl, preferably 2000 to 6000 SCF H_2/bbl over a catalyst selected from those recited above as useful for the optional hydro-treating step, in either a single stage or multi-stage process. Pure or plant hydrogen may be used. The permeate is converted into hydro-crackate and gas. Appropriate fraction of hydrocrackate may be blended into the REG mogas pool.

Alternatively the permeate may be hydrogenated for production of a distillate product or used directly as a chemical feedstock.

The selective membrane separation zone will operate under reverse osmosis, perstraction or pervaporation conditions, preferably pervaporation conditions.

The membrane separation zone can include the system described in U.S. Patent 3,370,102 which separates aromatics from saturates in a wide variety of feed mixtures including various petroleum fractions, naphthas, oils, and other hydrocarbon mixtures. Expressly recited in '102 is the separation of aromatics from kerosene. The process produces a permeate stream and a retentate stream and employs a sweep liquid to remove the permeate from the face of the membrane to thereby maintain the concentration gradient driving force. U.S. Patent 2,958,656 teaches the separation of hydrocarbons by type i.e. aromatics, unsaturated, saturated by permeating a portion of the mixture through a non-porous cellulose ether membrane and removing permeate from the permeate side of the membrane using a sweep gas or liquid. U.S. Patent 2,930,754 teaches a method for separating hydrocarbons by type, i.e. aromatics and/or olefins from gasoline boiling range mixtures by the selective permeation of the aromatics through certain cellulose ester non-porous membranes. The permeated hydrocarbons are continuously removed from the permeate zone using a sweep gas or liquid. U.S. Patent 4,115,465 teaches the use of polyurethane membranes to selectively separate aromatics from saturates via pervaporation.

U.S. Patent 4,914,064 teaches polyurea/urethane membranes and their use for the separation of aromatics from non-aromatic hydrocarbon. The membrane is characterized by possessing a urea index of at least 20% but less than 100%, an aromatic carbon content of at least 15 mole %, a functional group density of at least about 10 per 1000 grams of polymer and a C=O/NH ratio of less than about 8.

Thin film composites can be prepared either from suspension deposition as taught in U.S. Patent 4,861,628 or from solution deposition as taught in U.S. Patent 4,837,054.

The preparation of an anisotropic polyurea/urethane membrane is the subject of U.S. Patent 4,828,773 and U.S. Patent 4,879,044. The anisotropic membrane possesses a three layer structure, a thin dense layer generated at the film/support interface, a thin non-continuous skin which is generated at the membrane-quench solvent

interface and an open, porous structure which exists between the aforementioned thin dense layer and thin non-continuous skin layer.

Polyurethane imides are produced by endcapping a polyol selected from those recited above with a polyisocyanate also selected from those recited above followed by chain extending by reaction with a polyanhydride which produces the imide directly or with di or poly carboxylic acids which produce amic acid groups which can be chemically or thermally condensed/cyclized to the imide. Aliphatic and cycloaliphatic di- and polyisocyanates can be used as can be mixtures of aliphatic, cycloaliphatic, aralkyl and aromatic polyisocyanates. Polyurethane imide membranes and their use for aromatics/non-aromatics separation are the subject of U.S. Patent 4,929,358.

Isocyanurate crosslinked polyurethane membranes and their use for the separation of aromatics from non-aromatics is the subject of U.S. Patent 4,929,357.

Acrylic acid ester homopolymers or their copolymers with each other or with acrylic acid can also be used to make membranes for aromatics/saturates separations. The acrylic acid monomer units can be in free-acid form or partly or totally neutralized with metal or alkyl ammonium ions. The membranes can be covalently or ionically crosslinked.

Polyimide/aliphatic polyester copolymer membranes are examples of high temperature stable membranes which are preferred for use in this separation.

Membranes of the type are described in U.S. Patent 4,944,880 and U.S. Patent 4,990,275.

The polyester imide membranes are made from a copolymer comprising a polyimide segment and an oligomeric aliphatic polyester segment, the polyimide being derived from a dianhydride having between 8 and 20 carbons and a diamine having between 2 and 30 carbons and the

oligomeric aliphatic polyester being a polyadipate, a polysuccinate, a polymalonate, a polyoxalate or a polyglutarate.

The diamine is preferably diamine include phenylene diamine, methylene dianiline (MDA), methylene di-o-chloroaniline (MOCA), methylene bis (dichloroaniline) (tetrachloro MDA), methylene dicyclohexylamine (H_{12}-MDA), methylene dichlorocyclohexylamine (H_{12}MOCA), methylene bis (dichlorocyclohexylamine) (tetrachloro H_{12}MDA), 4,4'-(hexafluoroisopropylidene)-bisaniline (6F diamine), 3,3'-diaminophenyl sulfone (3,3' DAPSON), 4,4'-diaminophenyl sulfone (4,4' DAPSON), 4,4'-dimethyl-3,3'-diaminophenyl sulfone (4,4'-dimethyl-3,3' DAPSON), 2,4-diamino cumene, methyl bis(di-o-toluidine), oxydianiline (ODA), busaniline A, bisaniline M, bisaniline P, thiodianiline, 2,2-bis[4-(4-aminophenoxy) phenyl] propane (BAPP), bis[4-(4-aminophenoxy phenyl) sulfone (BAPS), 4,4'-bis(4-aminophenoxy) biphenyl (BAPB), 1,4-bis(4-aminophenoxy) benzene (TPE-Q), and 1,3-bis(4-aminophenoxy) benzene (TPE-R).

The dianhydride is preferably an aromatic dianhydride and is most preferably selected from the group consisting of pyromellitic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, 4,4'-(hexafluoroisopropylidene)- bis(phthalic anhydride), 4,4'-oxydiphthalic anhydride, diphenylsulfone-3,3',4,4'-tetracarboxylic dianhydride, and 3,3',4,4'-biphenyl-tetracarboxylic dianhydride.

Examples of preferred polyesters include polyethylene adipate, polyethylene succinate.

The polyesters used generally have molecular weights in the range of 500 to 4000, preferably 1000 to 2000.

In practice the polyester imide membrane may be synthesized as follows. One mole of a polyester polyadipate polysuccinate, polyoxalate, polyglutarate or polymalonate, preferably polyethylene adipate or polyethylene succinate, is reacted with two moles of the dianhydride, e.g., pyromellitic dianhydride to make a prepolymer in the endcapping step. One mole of this prepolymer is then reacted with

one mole of diamine, e.g., methylene di-o-chloroaniline (MOCA) to make a copolymer. Finally, heating of the copolymer at 260-300°C for about 1/2 hour leads to the copolymer containing polyester and polyimide segments. The heating step converts the polyamine acid to the corresponding polyimide via the imide ring closure with removal of water.

In the synthesis an aprotic solvent such as dimethylformamide (DMF) is used in the chain-extension step. DMF is a preferred solvent but other aprotic solvents are suitable and may be used. A concentrated solution of the polyamic acid/polyester copolymer in solvent is obtained. This solution is used to cast the membrane. The solution is spread in glass plate or a high temperature porous support backing, the layer thickness being adjusted by means of a casting knife. The membrane is first dried at room temperature to remove most of the solvent, then at 120°C overnight. If the membrane is cast on a glass plate it is removed from the casting plate by soaking in water. If cast on a porous support backing it is left as is. Finally, heating the membrane at 300°C for about 0.5 hours results in the formation of the polyimide. Obviously, heating to 300°C requires that if a backing is used the backing be thermally stable, such as teflon, fiber glass sintered metal or ceramic of a high temperature polymer backing.

As previously stated, the separation is practiced under reverse osmosis, perstractive or pervaporation conditions.

Reverse osmosis employs a membrane having pores in the range 0.0001 to 1.0 μm, preferably 0.0001 to 0.001μm and utilizing an applied pressure high enough to overcome the osmotic pressure of one of the components in the feed so as to form that component to permeate through the membrane. Typically reverse osmosis is conducted at temperatures ranging from 0 to 50°C at pressure of up to 1000 psig.

Perstraction involves the selective dissolution of particular components contained in a mixture into the membrane, the diffusion of those components through the membrane and the removal of the diffused components from the downstream side of the membrane by use of

a liquid sweep stream. In the perstractive separation of aromatics from saturates in petroleum or chemical streams (particularly heavy cat naphtha streams) the aromatic molecules present in the feedstream dissolve into the membrane film due to similarities between the membrane solubility parameter and those of the aromatic species in the feed. The aromatics then permeate (diffuse) through the membrane and are swept away by a sweep liquid which is low in aromatics content. This keeps the concentration of aromatics at the permeate side of the membrane film low and maintains the concentration gradient which is responsible for the permeation of the aromatics through the membrane.

The sweep liquid is preferably a saturated hydrocarbon liquid with a boiling point much lower or much higher than that of the permeated aromatics. Provided the sweep liquid boiling range is much lower or higher than that of the permeated aromatics, the presence of aromatics in that sweep would not affect the permeate aromatics concentration gradient, (i.e., they would be in a different boiling range and therefore be different aromatics). This would facilitate separation, as by simple distillation. Suitable sweep liquids, therefore, would include, for example, C_3 to C_6 saturated hydrocarbons and lube basestocks (C_{15}-C_{20}).

The perstraction process is run at any convenient temperature, preferably as low as possible.

The choice of pressure is not critical since the perstraction process is not dependent on pressure, but on the ability of the aromatic components in the feed to dissolve into and migrate through the membrane under a concentration driving force. Consequently, any convenient pressure may be employed, the lower the better to avoid undesirable compaction, if the membrane is supported on a porous backing, or rupture of the membrane, if it is not so supported.

If C_3 or C_4 sweep liquids are used at 25°C or above in liquid state, the pressure must be increased to keep them in the liquid phase.

Pervaporation, by comparison, is run at generally higher temperatures than perstraction with the feed being in either liquid or vapor form and relies on vacuum or sweep gas on the permeate side to evaporate or otherwise remove the permeate from the surface of the membrane and maintain the concentration gradient driving force which drives the separation process. As in perstraction, the aromatic molecules present in the feed dissolve into the membrane film, migrate through said film and reemerge on the permeate side under the influence of a concentration gradient. While pervaporation separation of aromatics from saturates can be performed at a temperature of about 25°C for the separation of benzene from hexane, the separation of heavier aromatic/saturate mixtures, such as heavy cat naphtha, require that higher temperatures of at least 80°C and higher, preferably at least 100°C and higher, more preferably 120°C and higher (up to about 170 to 200°C and higher) be used, the maximum upper limit being that temperature at which the membrane is physically damaged. Vacuum on the order of 1-200 mm Hg is pulled on the permeate side. The vacuum stream containing the permeate is cooled to condense out the highly aromatic permeate. Condensation temperature should be below the dew point of the permeate at a given vacuum level.

The membrane itself may be in any convenient form utilizing any convenient module design. Thus, sheets of membrane material may be used in spiral wound or plate and frame permeation cell modules. Tubes and hollow fibers of membranes may be used in bundled configurations with either the feed or the sweep liquid (or vacuum) in the internal space of the tube or fiber, the other material obviously being on the other side.

Most conveniently, in perstraction the membrane used is in a hollow fiber configuration with the feed introduced on the exterior side of the fiber, the sweep liquid flowing on the inside of the hollow fiber to sweep away the permeated highly aromatic species, thereby maintaining the desired concentration gradient. The sweep liquid, along with aromatics contained therein, is passed to separation means, typically distillation means, however, if a sweep liquid of low enough molecular weight is used, such as liquefied propane or

butane, the sweep liquid can be permitted to simply evaporate, the liquid aromatics being recovered and the gaseous propane or butane (for example) being recovered and reliquefied by application of pressure or lowering the temperature.

Practice of the present invention offers the following advantages.

In situations where the refiner does not have sufficient capacity to accommodate the full HCN stream, the membrane separation could provide a lower investment alternative than a revamp or grass-roots hydrocracker, particularly if existing hydrotreaters could be used to finish the retentate stream when necessary.

The overall hydrogen consumption and hydrogen pressure requirements should be lower for the present processing scheme. This is because the molecules diverted by the membrane unit from the hydrocracker (i.e. the retentate) are subjected to lower pressure hydrotreating and also because the membrane separation has removed much of the sulfur and nitrogen containing species from this stream (retentate) and placed those molecules into the permeate sent to the hydrocracker where they can be subjected to higher pressure hydrogenation.

The membrane-hydrotreating process should result in overall higher yields of liquid hydrocarbons as the mainly saturates retentate portion of the HCN-LCCO stream does not pass through the hydrocracker wherein some conversion to gas might occur.

The membrane-hydrotreating scheme should result in less overall reduction in product value since formerly mogas HCN molecules are converted to hydrocrackate and some distillate product rather than hydrocrackate only. Product upgrade should also result if low value LCCO components are included in the membrane feed for separation to give higher value distillate products. In the future REG environment, wherein distillate margins are expected to rival those of mogas, these improvements and benefits would be even greater.

Figure 1 presents the typical current processing stream. Effluent from the cat cracker unit is sent via line 1 to a fractionator (2) wherein the effluent is split into light and intermediate cat naphtha (3) and heavy cat naphtha (4) which are blended into the mogas pool (5). Light cat cycle gas oil is sent via line (6) to a hydrocracker (7) for conversion into hydrocrackate (8) and gas (9).

Figure 2 presents a variation of the current typical process stream modified to produce reduced emissions gasoline. Effluent from a cat cracker is sent via line 1 to a fractionator (2) wherein it is split into light and intermediate cat naphtha which is sent via line (3) to the reduced emissions gasoline pool (4). Heavy cat naphtha boiling in the 300°F+ range (line 5) and light cat cycle oil (line 6) are sent to a hydrocracker (7) for conversion into gas (8) and hydrocrackate (9).

Figure 3 presents the present invention.

Effluent from a cat cracker is sent via line 1 to a fractionator 2 wherein it is split into light and intermediate cat naphtha sent via line 3 to the reduced emissions gasoline pool 4. Heavy cat naphtha boiling in the 300-450°F range or broad cut 300-550°F range is sent via line 5 to membrane unit 6. Light cat cycle oil is recovered from fractionator 2 via line 7. LCCO is sent via line 7 to the hydrocracker 8. In membrane unit 6 the HCN is separated into a saturates rich retentate which is sent via line 9 to optional hydrotreater 10 for finishing into jet blending stock or distillate (11) or bypasses the hydrotreating and is sent via line 9a directly to the jet or distillate pool. A permeate (12) rich in aromatics, polars and heteroatom compounds from the membrane separation unit is sent to the hydrocracker 8 wherein it along with the LCCO from line 7 is converted into hydrocrackate (13) and gas (14).

CLAIMS

1.   A process for maximizing hydrocarbon feed utilization in the production of reduced emissions gasoline said process comprising the steps of:

(a)   fractionating cat cracker effluent into a reduced emissions gasoline blending stream, a heavy cat naphtha stream and a light cat cycle oil stream;

(b)   passing the heavy cat naphtha to a selective membrane separation unit;

(c)   recovering from the membrane separation unit an aromatics-, sulfur-, and other heteroatom-rich permeate and a saturates-rich retentate;

(d)   passing the saturates rich retentate to a jet fuel or distillate pool, and

(e)   recovering the aromatics, sulfur, and other heteroatom rich permeate for further treatment.

2.   The process of claim 1 wherein the saturates rich retentate recovered from the membrane separation unit is subjected to treatment in a hydrotreater prior to being sent to the jet fuel or distillate pool.

3.   The process of claim 1 or claim 2 wherein the heavy cat naphtha fraction sent to the membrane separation units is a broad cut fraction boiling in the range of from 300°F to 550°F (176.7 to 287.8°C).

4.   The process of any one of claims 1 to 3 wherein the aromatics-, sulfur-, and other heteroatom-rich permeate is hydrocracked for the production of hydrocrackate and gas.

5.   The process of any one of claims 1 to 3 wherein the aromatics-, sulfur-, and other heteroatom-rich permeate is

hydrogenated for the production of a distillate product or chemical feedstock.

6.   The process of any one of claims 1 to 5 wherein the membrane separation unit is operated under reverse osmosis, perstraction, or pervaporation conditions.

15.

Application number GB 9312557.3	

Relevant Technical fields

(i) UK Cl (Edition   L   )   C5E (ESA)

(ii) Int Cl (Edition   5   )   C10G

Databases (see over)

(i) UK Patent Office

(ii)   ONLINE DATABASES: WPI, CLAIMS

Search Examiner

R J WALKER

Date of Search

27 AUGUST 1993

Documents considered relevant following a search in respect of claims   1-6

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	US 5098570 (SCHUKER) - column 2 lines 52-65; column 7 lines 61-66	1
X	US 5096592 (SCHUKER) - column 1 lines 36-41; column 8 lines 21-26	1
X	US 5095171 (FEIMER ET AL) - column 4 lines 42-59	1

Category	Identity of document and relevant passages	Relevant to claim(s)